Room Temperature Na-ion Battery Development

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DOE Office of Electricity Energy Storage Program – Imre Gyuk Program Manager.

OE Energy Storage Systems Program Review

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Outline

1. **Introduction**
   - **Advantages and challenges of Na-ion batteries**
   - **Current status and perspective**
2. **Overview of our previous work**
3. **Progress of FY14**

   i) Optimization of $Na_{0.44}MnO_2$ (C)-hard carbon (A) chemistry

   ii) Development of phosphate ($Na_3V_2(PO_4)_3$) cathode

   iii) Exploration of Prussian blue cathode materials
4. **Summary and Future work**

Why Na-ion Batteries

Sodium-ion batteries are a type of reusable battery that uses sodium-ions as its charge carriers. (http://en.wikipedia.org/wiki/Sodium-ion_battery)

Advantages:

- Na-ion batteries are very similar to Li-ion batteries in many ways
- Potentially can have a high energy density

  e.g. >300 Wh/kg (material level estimation),

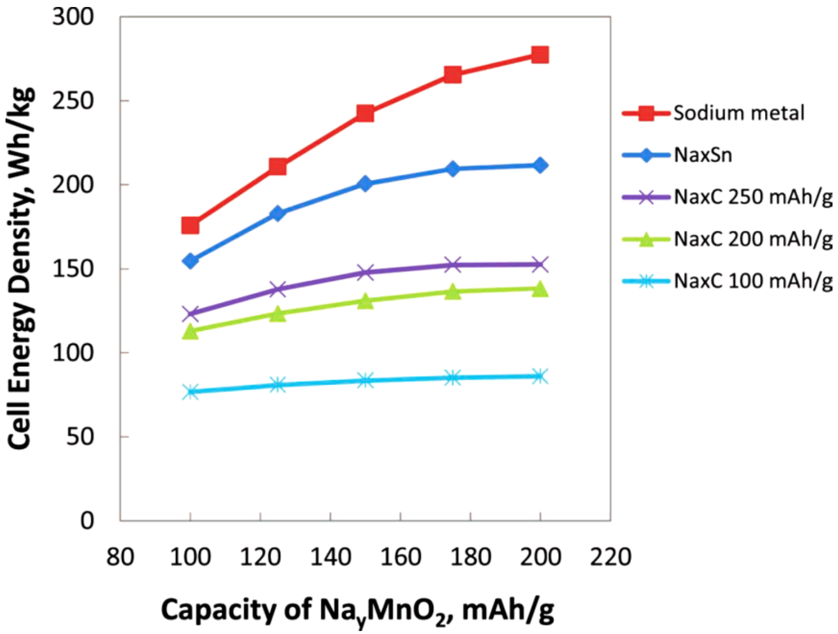
  ~150 Wh/kg (cell level estimation)

- Operate at room temperature
- Na sources are more abundant than Li and geographically uniformly distributed

  Li_2CO_3 (~$5000/ton)

  http://www.lithiumsite.com/market.html

  Na_2CO_3 (~$150/ton)



Energy densities for various Na-ion systems

*calculated using the BatPaC model software package.
**average discharge voltage =3.3V, power/energy ratio =2.
***Standard Li-ion cell energy density calculated with the same technique range from 160 to 210 Wh/kg.

1. M. d. Slater, et al. Adv. Funct. Mater. 2013, 23, 947.
2. S. P. Ong, et al. Energy Environ. Sci.. 2011, 4, 3680.

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Challenges

- Na-ion is ~30% larger than Li-ion in diameter and ~2 times heavier.

  ~ lower gravimetric capacity than Li-ion batteries.
- Na metal standard electrode potential is ~0.3V higher than Li.

  Low cathode voltage and high anode voltage; low cell voltage
- Na metal is more active than Li

Cathode, Anode, Electrolyte

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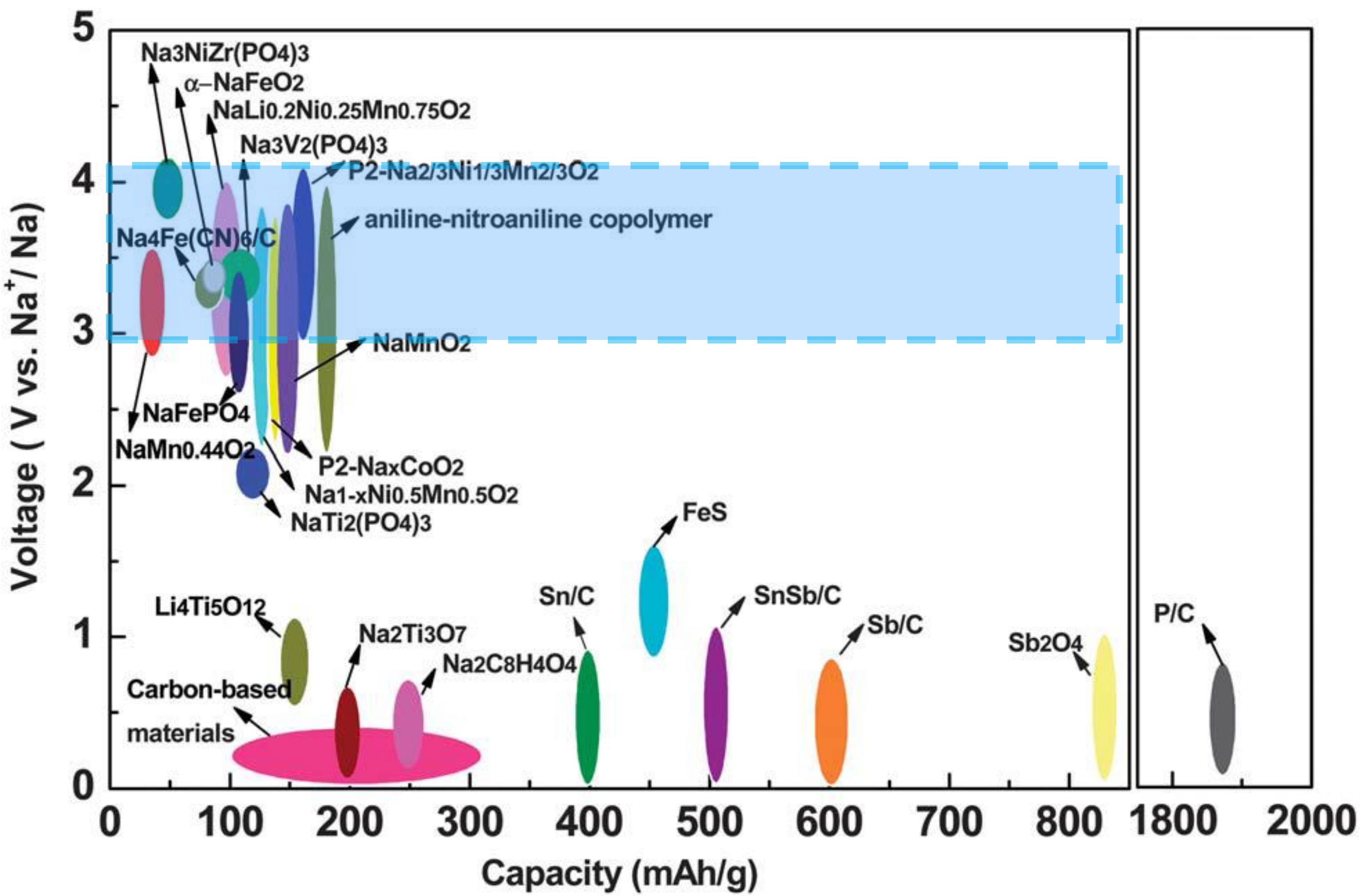
Current Status

Chart of cathode and anode materials for Na-ion batteries



H.L. Pan, et al. Energy Environ. Sci. 2013, 6, 2338

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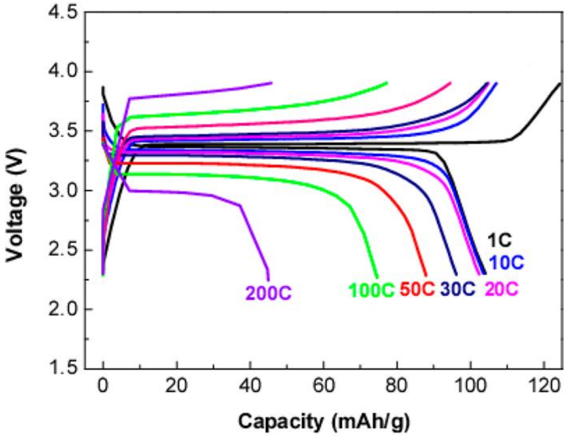
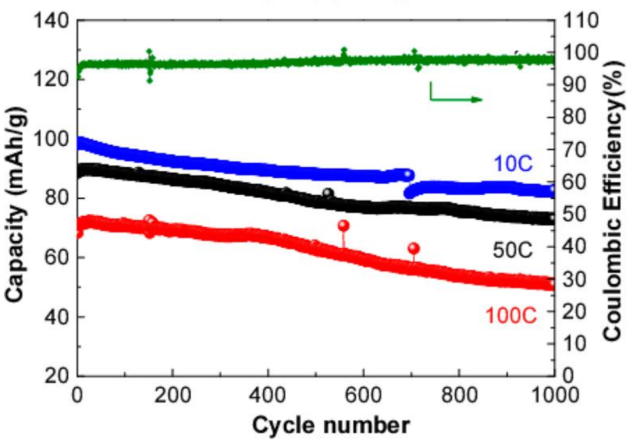
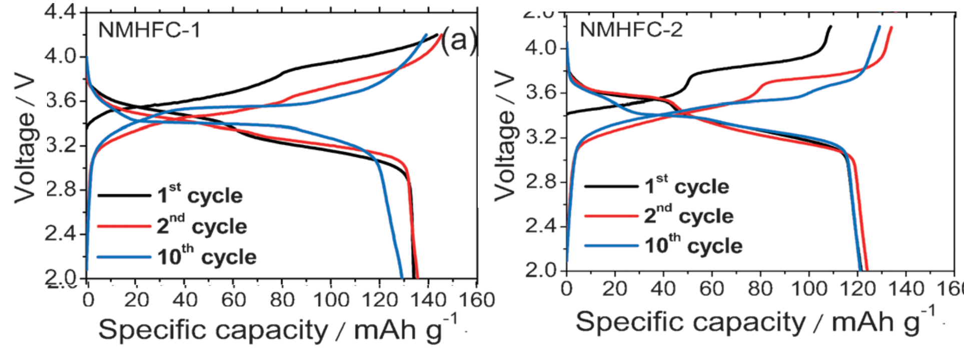
Current Status

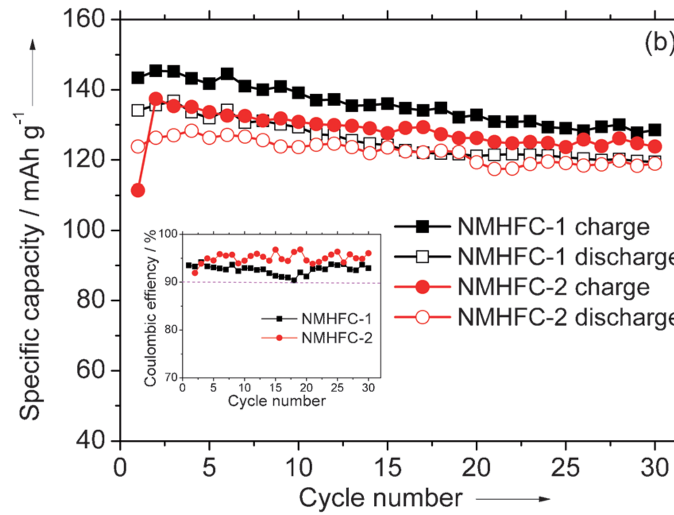
$Na_3V_2(PO_4)_3$





$Na_{1.72}MnFe(CN)_6$ and $Na_{1.40}MnFe(CN)_6$





$Na_3V_2(PO_4)_3$ and Prussian blue materials are promising cathodes with high capacites (~120 mAh/g), good cycling stability, and rate performance.

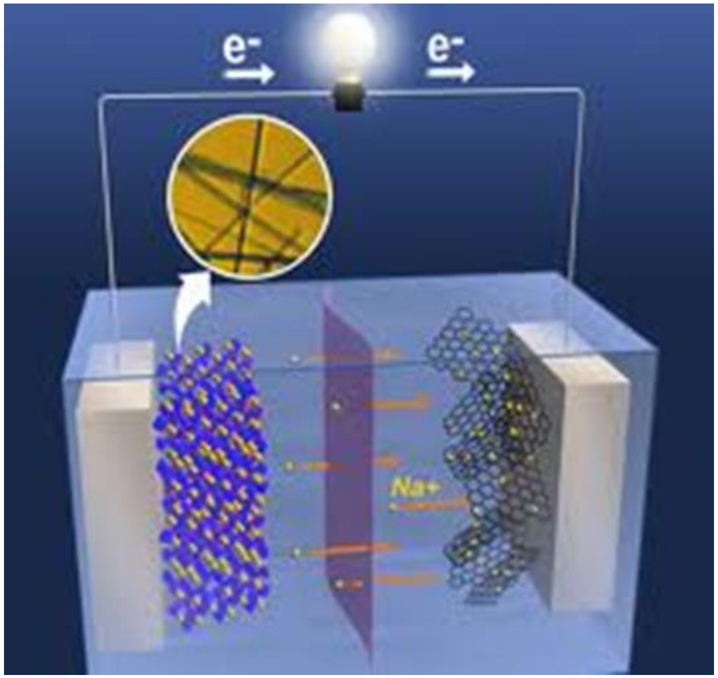
1. C.B.. Zhu, et al. Nano Lett. 2014, 14, 2175.
2. L. Wang, et al. Angew. Chem. Int. Ed. 2013, 52, 1964.

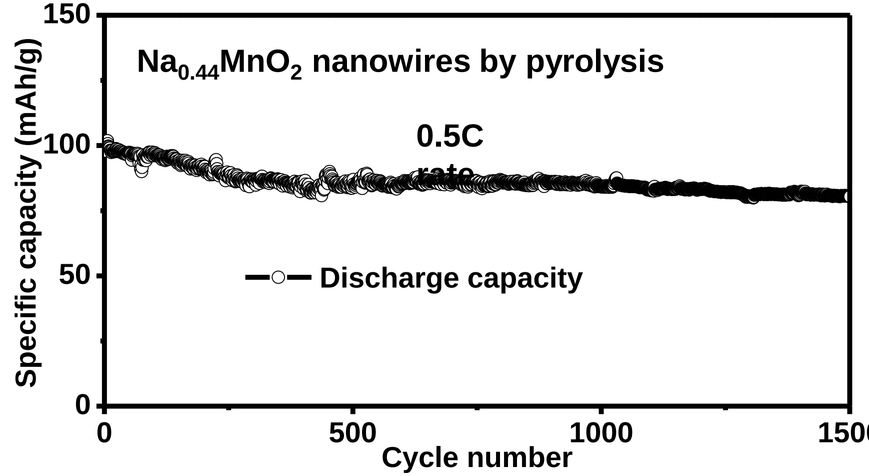
Our Perspective

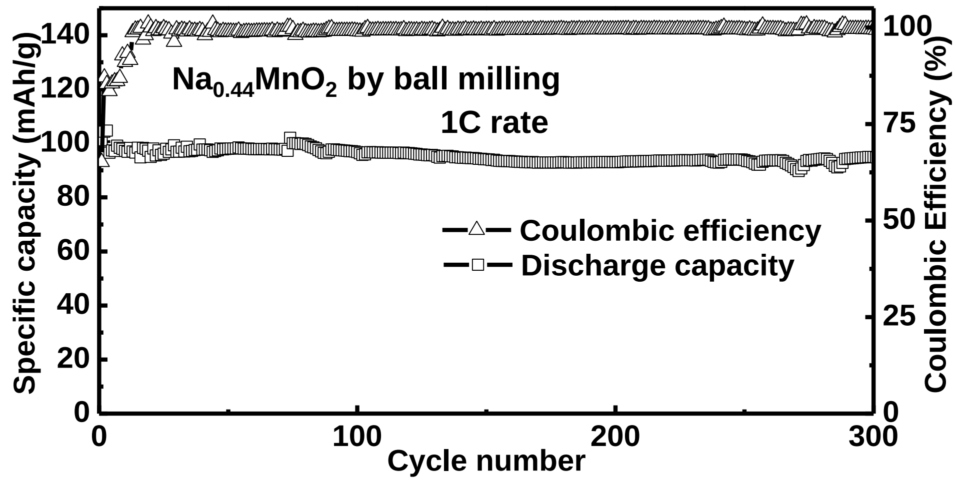
PNNL will demonstrate potentially low cost full cell Na-ion batteries with high capacity and long cycling stability for grid scale applications

Overview of Our Previous Work

$Na_{0.44}MnO_2$ half cell







- $Na_{0.44}MnO_2$ nanowires synthesized using a polymer-pyrolysis method showed excellent cycling stability in half-cell design with ~79% capacity retention over 1500 cycles at 0.5C rate.
- The $Na_{0.44}MnO_2$ obtained by ball milling method has good cycling stability with ~95% capacity retention over 300 cycles at 1c rate (1C = 120 mA/g).

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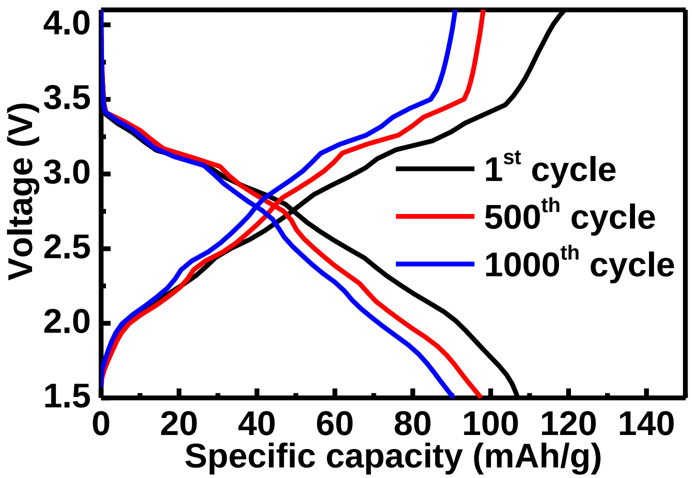
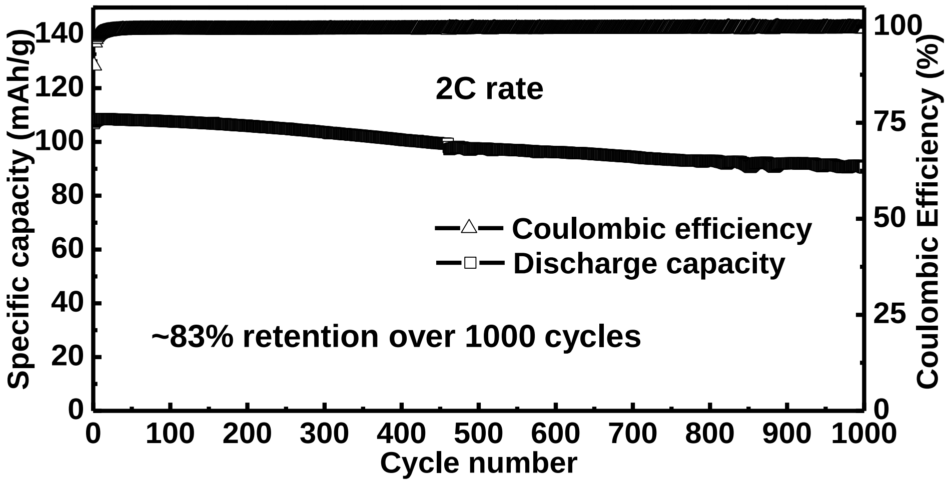
Y. L. Cao, et al. Adv. Mater., 2011, 23, 3155

Overview of Our Previous Work

$Na_{0.44}MnO_2$ – hard carbon full cell





- The full cell of $Na_{0.44}MnO_2$ cathode and hard carbon anode can have excellent cycling stability and rate performance.
- It can have an initial capacity of ~108 mAh/g (corresponding energy density is ~280 Wh/kg) and ~83% capacity retention over 1000 cycles at 2C rate (1C = 120 mA/g).

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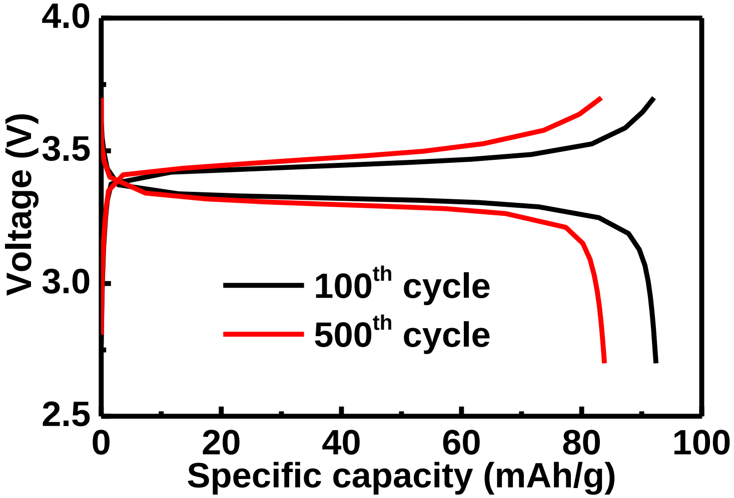
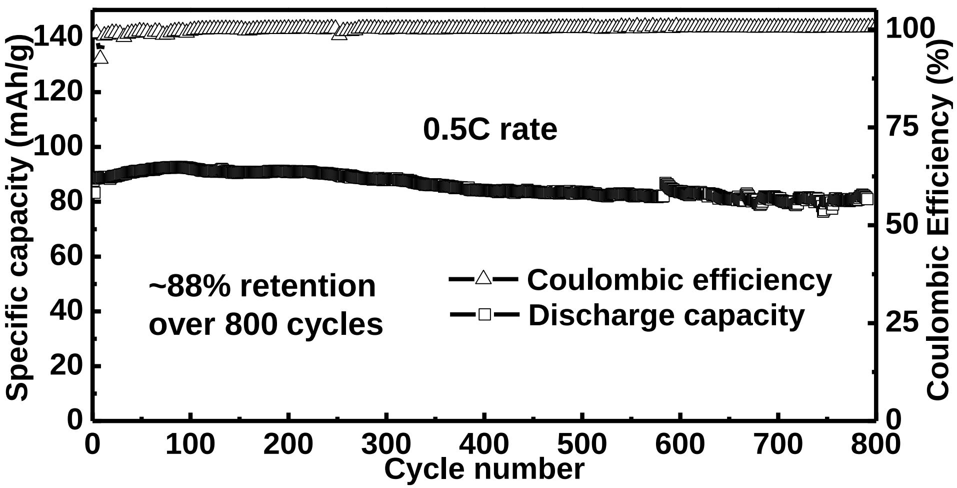
Overview of Our Previous Work

$Na_3V_2(PO_4)_3$–carbon cathode





- $Na_3V_2(PO_4)_3$ has a high discharge voltage at ~3.2 V versus Na metal
- It has a capacity of ~92 mAh/g at 0. 5C rate and good cycling stability with ~88% capacity retention over 800 cycles (1C = 120 mA/g).

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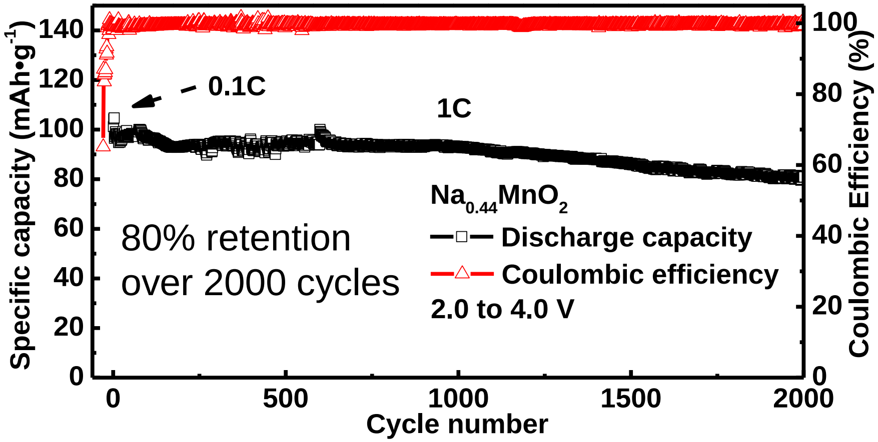
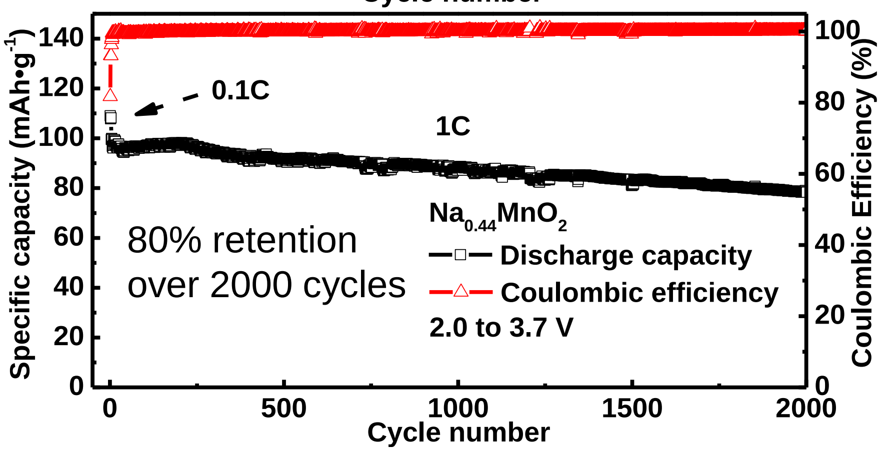
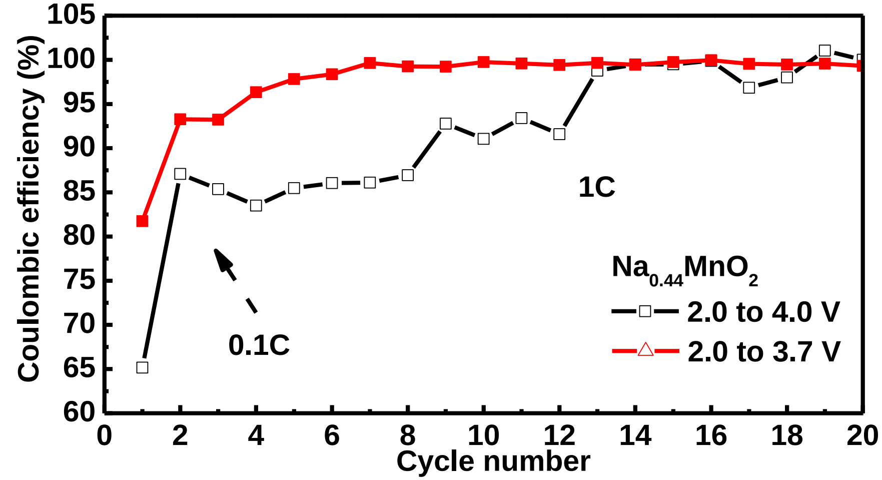
i) Optimization of $Na_{0.44}MnO_2$-Hard Carbon Chemistry

Optimize the voltage window to improve first cycle Coulombic efficiency

$Na_{0.44}MnO_2$ half cell







Enlarged figure to show the Coulombic efficiency in the first 20 cycles.

- The first cycle Coulombic efficiency is improved to >80% when cycling between 2 to 3.7V.
- The capacity and cycling stability are almost similar (1C = 120 mA/g).

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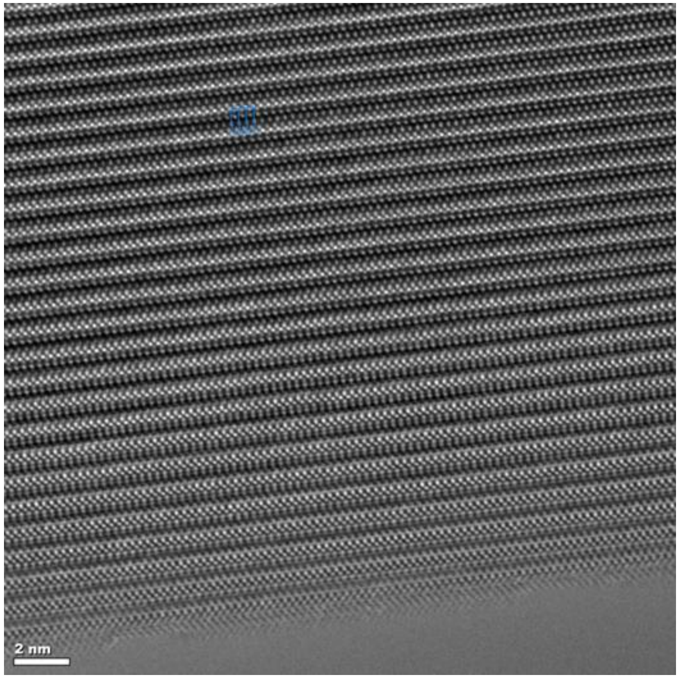
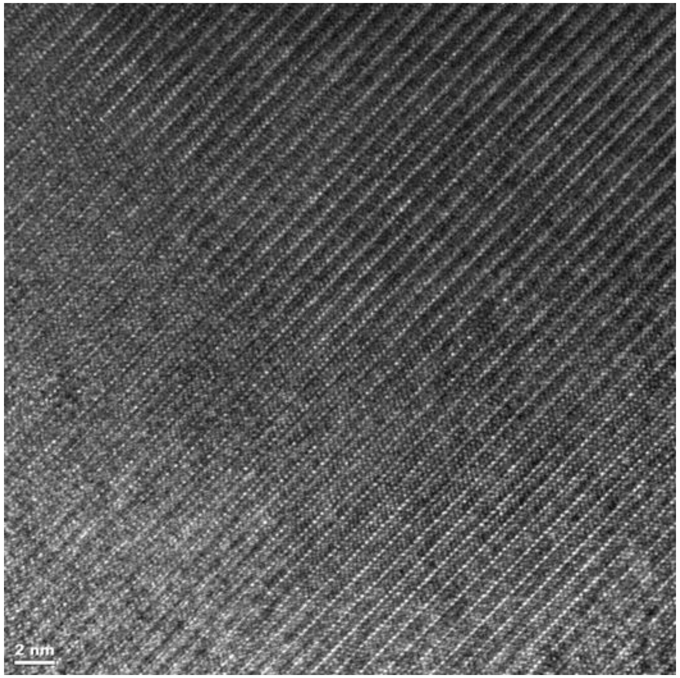
Structure Characterization of $Na_{0.44}MnO_2$

TEM characterization of the $Na_{0.44}MnO_2$ cathode before and after cycling

pristine



After 1000 cycles



- The structure of $Na_{0.44}MnO_2$ is very stable upon cycling. Its structure doesn't change much even after 1000 cycles. It remains to be single crystal.

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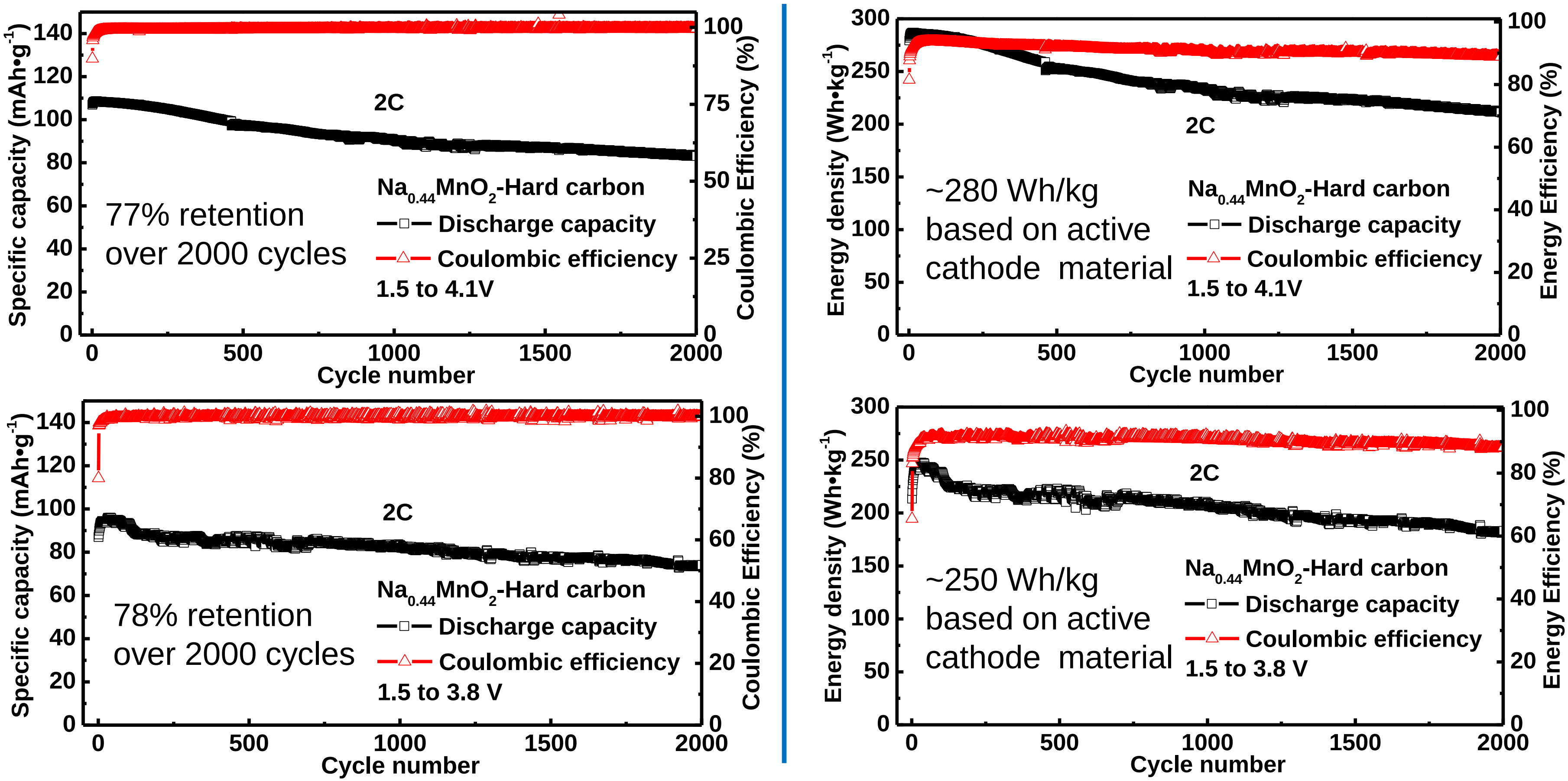
$Na_{0.44}MnO_2$-Hard Carbon Full Cell

The effect of different voltage window to the full cell performance



- The specific capacity and energy density are slightly lower when the full cell cycles between 1.5 to 3.8V.
- The cycling stability are almost similar (1C = 120 mA/g).

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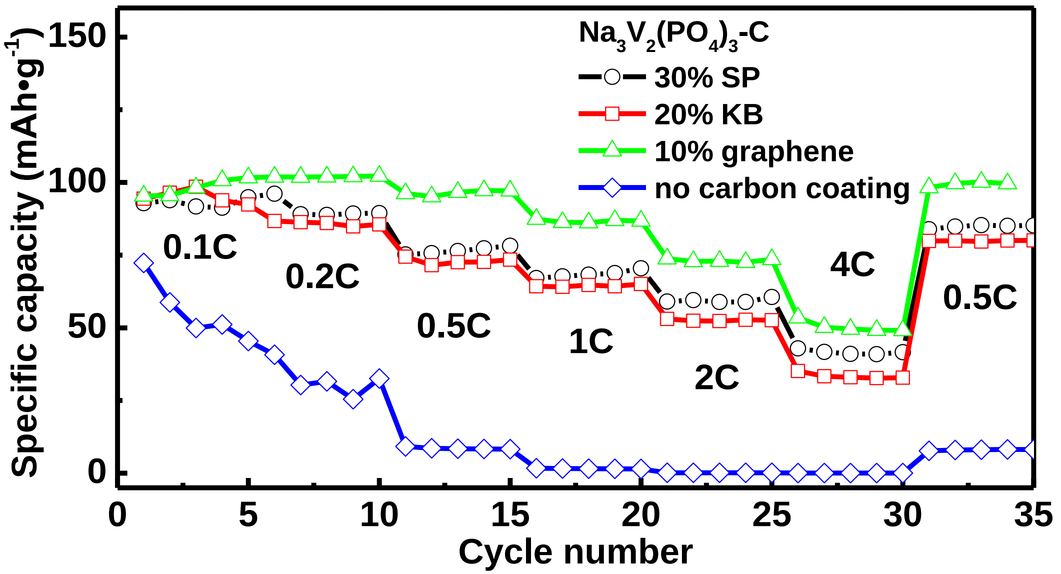
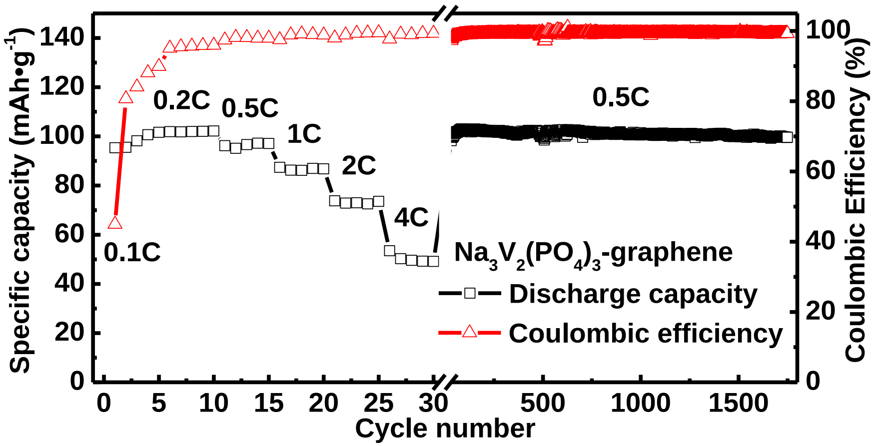
ii) Development of $Na_3V_2(PO_4)_3$ Cathode

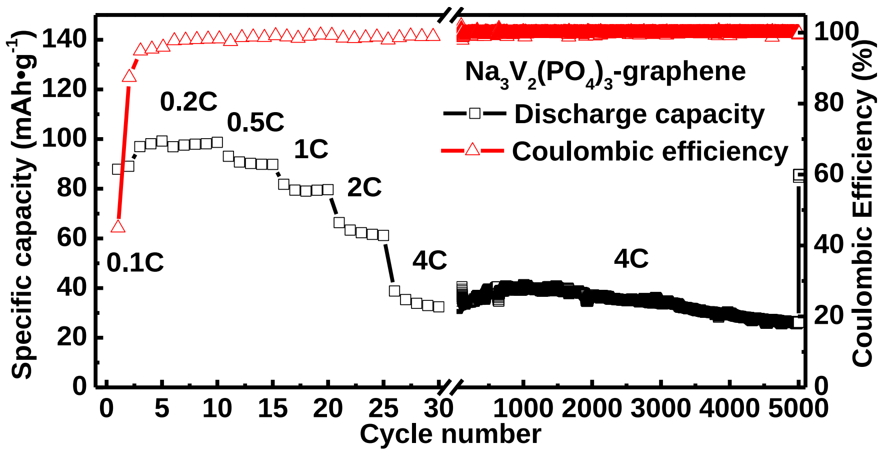
$Na_3V_2(PO_4)_3$–graphene composite cathode



- Carbon coating is necessary to get good rate performance
- The use of graphene can improve the rate performance of $Na_3V_2(PO_4)_3$ (1C = 120 mA/g).

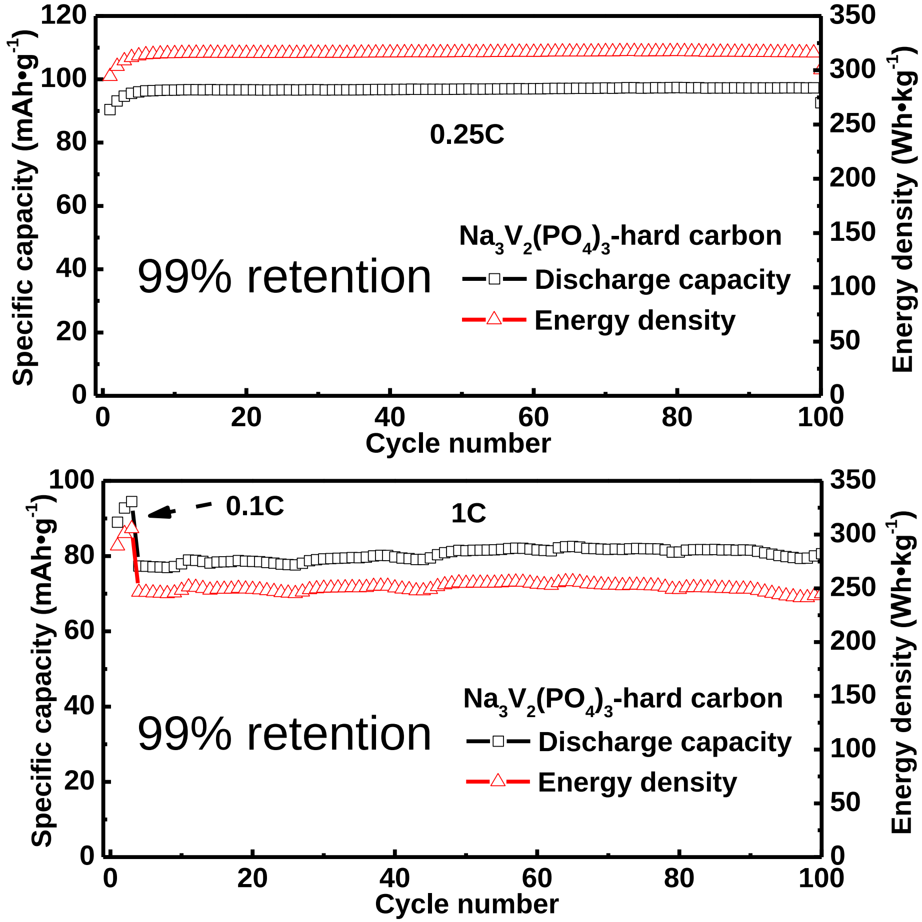
Cycling stability of $Na_3V_2(PO_4)_3$ Cathode





- $Na_3V_2(PO_4)_3$–graphene composite shows good cycling stability in half cell
  - ~97% capacity retention over 1600 cycles at 0.5C rate (cycled for 8 months). (1C = 120 mA/g)
  - ~63% capacity retention over 5000 cycles at 4C rate. When switch back to 0.5C rate, the capacity can be recovered to ~85 mAh/g.
- The first cycle Coulombic efficiency is ~50% at 0.1C rate.
- The Coulombic efficiency at stable cycling is ~99.3% at 0.5C and ~99.9% at 4C rate.

$Na_3V_2(PO_4)_3$-Hard Carbon Full Cell



- ➢ $Na_3V_2(PO_4)_3$-hard carbon full cell can have a capacity of ~97 mAh/g at 0.25C rate and ~80 mAh/g at 1C rate. The energy density based on active cathode material is ~315 Wh/kg and ~250 Wh/kg, respectively.
- ➢ It has good cycling stability with ~99% capacity retention over 100 cycles.

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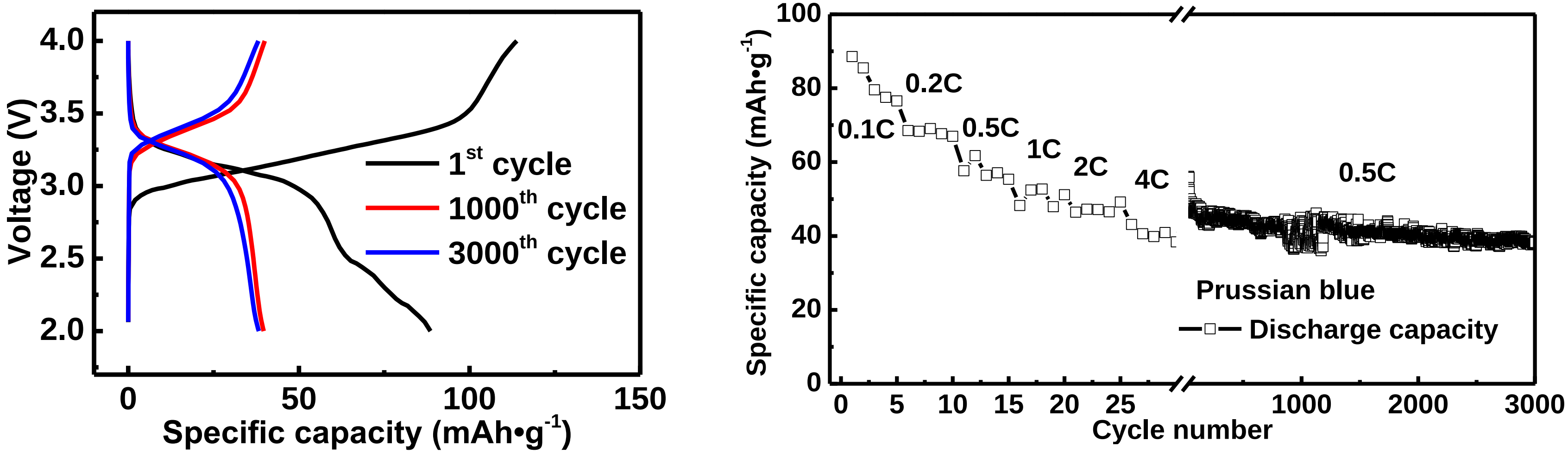
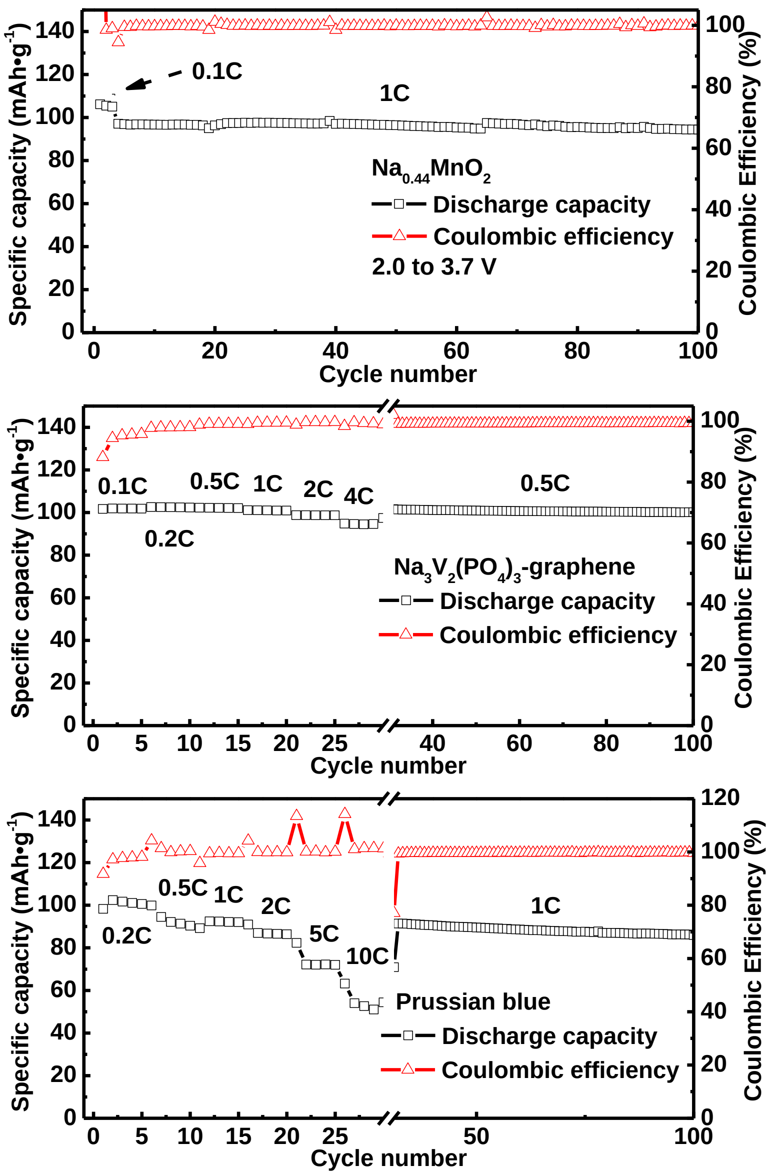
iii) Exploration of Prussian blue cathodes

CuHCFe from Stanford



- The capacity is ~88 mAh/g at 0.1C and ~56 mAh/g at 0.5C rate (1C = 100 mA/g).
- It has excellent cycling stability with the capacity retention of ~68% (38 mAh/g) over 3000 cycles. at 0.5C.
- The first cycle Coulombic efficiency is ~77%. The Coulombic efficiency is ~99.8% at stable cycling at 0.5C rate.

Improvement of Cathode Coulombic Efficiency



- The cathode materials' Coulombic efficiency, especially the first cycle efficiency, can be greatly improved.
  - The Coulombic efficiency of $Na_{0.44}MnO_2$ is 99% after the 3rd cycle at 0.1C rate. (1C = 120 mA/g)
  - The first cycle Coulombic efficiency of $Na_3V_2(PO_4)_3$-graphene is ~88% at 0.1C rate. It quickly increases to 98%. The Coulombic efficiency can be ~99.8% at stable cycling at 0.5C. (1C = 120 mA/g)
  - The first cycle Coulombic efficiency of Prussian blue material can be ~91% at 0.2C rate. It quickly increases to 99%. The Coulombic efficiency can be ~99.8% at stable cycling at 1C. (1C = 120 mA/g)

Summary

- Potentially low cost and scalable methods have been developed for the synthesis of metal oxide, phosphate, and Prussian blue cathodes for room-temperature Na-ion batteries.
- The full cell of $Na_{0.44}MnO_2$ and commercial hard carbon has a high capacity of ~108 mAh/g at 2C rate and excellent cycling stability with ~77% capacity retention over 2000 cycles.
- The phosphate cathode has a high capacity of ~100 mAh/g at low charge/discharge rate and excellent cycling stability with ~97% capacity retention over 1600 cycles.
- Prussian blue as a new cathode material is under exploration . A capacity of ~100 mAh/g was obtained at 0.2C rate.
- The Coulombic efficiency of cathode materials can be improved.

Future work

- Development of stable Na-ion battery anode materials of high capacity and high Coulombic efficiency.
- Demonstration of high performance $Na_3V_2(PO_4)_3$ full cells
- Development of Prussian blue cathode materials
- Material scale up to large cell (pouch cells or 18650 cells) fabrication
- Safety (heat generation) assessments and cost estimation (component cost).

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